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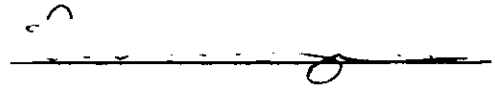

7/25/68

SOME IMPORTANT INORGANIC NITROGEN AND PHOSPHORUS SPECIES IN GEORGIA SALT MARSH

A THESIS

Presented to

The Faculty of the Division of Graduate

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Peter Robert Maye, III

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SPECIES IN GEORGIA SALT MARSH

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Chairman

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SUMMARY

Thirteen cores were taken at various locations in the marshes in the Savannah River, Ogeechee River, and Skidaway Island areas of Coastal Georgia. Sediments and interstitial waters from the cores were analyzed for the important inorganic nitrogen and phosphorus species.

The interstitial waters contained ammonium and phosphate in varying concentrations and in general the concentrations increased with depth in core.

Both exchangeable and nonexchangeable ("fixed") ammonium were found in the marsh sediments. The amount of exchangeable ammonium was very low in all cases. The fixed ammonium was more abundant and averaged about five times greater than the exchangeable form. As expected, both exchangeable and fixed ammonium present in the sediment were dependent on the amount of clay present.

The three important inorganic phosphorus species Al-PO_4, Fe-PO_4, and Ca-PO_4 were found in the marsh sediments in varying abundances. It is apparent that both grain size and salinity may influence the relative amounts of the phosphate species present in a given sample.

The major source of both inorganic nitrogen and phosphorus in the sediments is the marsh grass *Spartina alterniflora*.

CHAPTER I

INTRODUCTION

Two of the most important chemical processes which occur in the salt marsh environment are the cyclic regenerations of nitrogen and phosphorus (Bailey, 1968; Bremner, 1965; Rittenberg et al., 1955). The present work is a study of the occurrence and distribution of the important inorganic nitrogen and phosphorus forms at various locations in a Georgia salt marsh. A particular problem involving the fixation of ammonium by clay minerals was examined. Rittenberg et al. (1955), studying the nitrogen distribution in basin sediments, found that a decrease in organic nitrogen with depth was not balanced by a sufficient increase in inorganic nitrogen. It was concluded that ammonia was being lost to the overlying waters. The present study, however, examines the possibility that an uptake of nitrogen by clay minerals may be responsible for the discrepancy.

No important studies on the occurrence of nitrogen and phosphorus in marshes have been previously made. However, extensive studies have been made by soil scientists (Bailey, 1968; Bremner, 1965; Freney, 1964; Harter, 1969; and others), and the chemical and biochemical reactions of nitrogen and phosphorus in soils are well established. Fortunately, important processes such as ammonification, nitrification, and nitrogen and phosphorus fixation are similar whether they occur in marshes or in soils.

Inorganic Nitrogen

In most soils the inorganic combined nitrogen is in the form of ammonium and nitrate. These forms undergo various reactions brought about by bacterial activity. Such reactions are highly dependent on environmental parameters such as oxygen availability, pH, Eh, temperature, and organic content. Figure 1 is a Eh-pH diagram for the inorganic nitrogen species. The diagram was calculated from free energy data given by Garrels and Christ (1965).

Ammonification, one of the important reactions, consists of the bacterial decomposition of plankton and other organic matter with ammonia as a product. Ammonifying bacteria can be both aerobes and anaerobes and thus ammonification is independent of Eh. The pH does influence the process, however, and acidification tends to be a depressant. The temperature effect is such that the rate of process increases with increasing temperature to reach an optimum at 40° to 60°C (Alexander, 1961).

Where oxygen is present ammonium forms undergo another bacterial reaction known as nitrification. The reaction consists of two distinct steps. First, the ammonium is oxidized to nitrite by bacteria of the *Nitrosomonas* group. The reaction is optimum in the pH range 7.5 to 8.8 and intermediate unstable products between ammonium and nitrite are probably formed (Hofman and Lees, 1953). The importance of any intermediate products has not been established. Although *Nitrosomonas* is by far the most important nitrifying group, certain heterotrophic bacteria have been found which are capable of oxidizing ammonia to nitrite

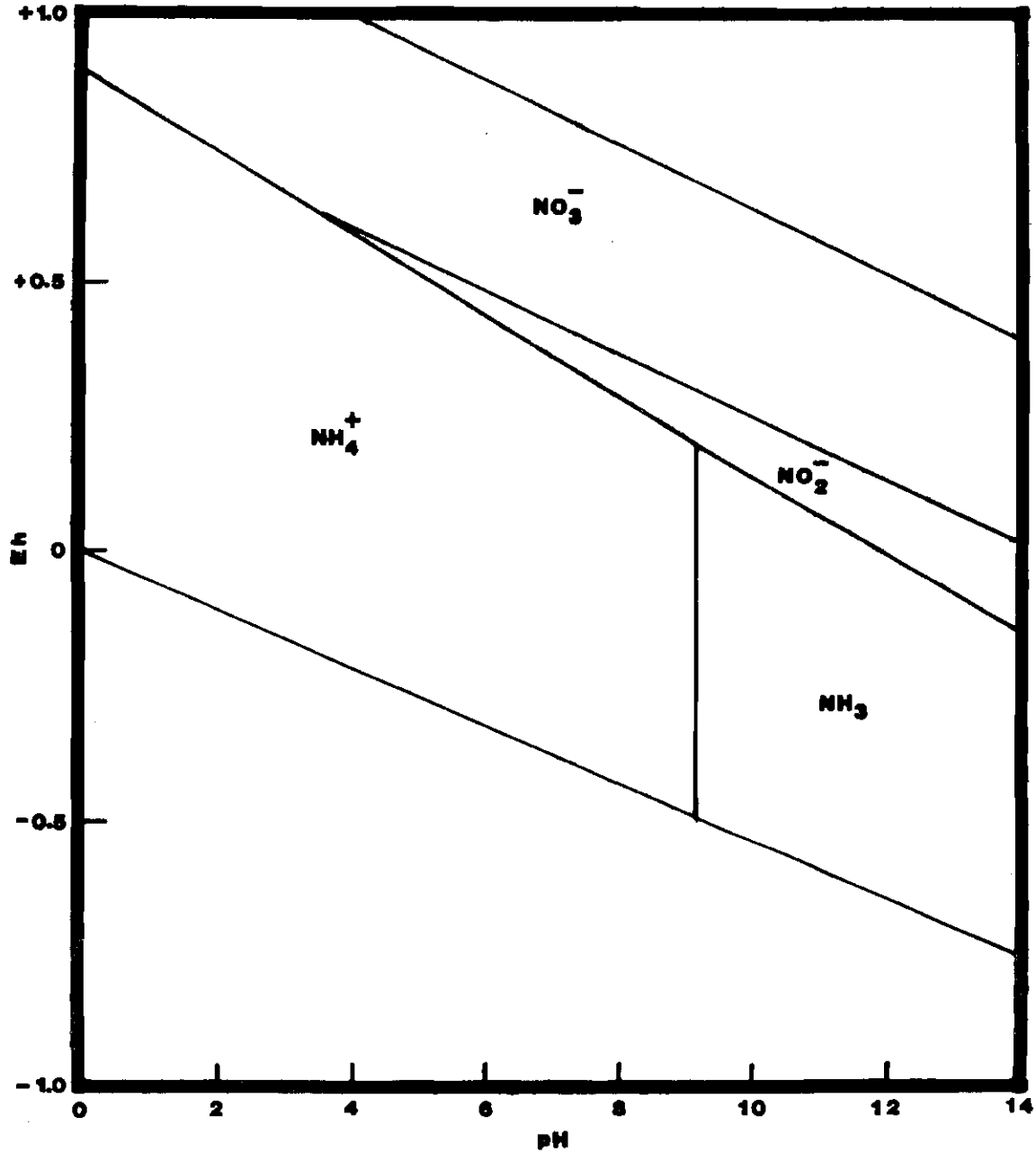

Figure 1. Eh vs. pH Diagram for Nitrogen Species

(Eylar and Schmidt, 1959). The amount of nitrite formed is quite small compared to that from *Nitrosomonas*. However, these heterotrophic bacteria are abundant in nature and might contribute substantially to the nitrogen cycle.

The second step of nitrification is the oxidation of nitrite to nitrate by the bacteria of the *Nitrobacter* group. In a wide variety of soils the optimum oxidation rate requires the presence of about 5 ppm each of magnesium and phosphorus and 7 gm of iron per liter (Lees and Simpson, 1957). It is also noted that ammonia will inhibit the reaction and thus heavy metastable nitrite concentrations are often found in areas of high ammonia content. Lees and Simpson (1957) give a good study on the metabolism of the *Nitrobacter* group. As in nitrite production, heteratrophs capable of nitrate formation have been found (Eylar and Schmidt, 1959).

In areas of little or no available oxygen, aerobic bacteria which have adapted to the utilization of nitrate and nitrite carry on a reaction known as denitrification (Bremner, 1965). The nitrite and nitrate are reduced to ammonia and subsequently converted to molecular nitrogen. It is important to note that no biological process has been found by which molecular nitrogen is formed directly from ammonia. Nitrate or nitrite must be present. Most of the denitrifying activity is produced by the bacteria genera *Pseudomonas, Achromoleacter, Bacillus,* and *Micrococcus*. Denitrification occurs only in anaerobic conditions. However, there must be an associated aerobic environment where nitrite and nitrate can be produced. The pH controls the proportions of the

different gasses liberated. Above pH 6, molecular nitrogen is the dominant product. Temperature also affects the process and the transformation of nitrate to molecular nitrogen increases with temperature to an optimum at 25°C or above. The growth of these bacteria is not dependent on the reduction of nitrate and thus they must have a source of energy such as available organic matter. In fact the availability or organic matter is probably the limiting factor in the occurrence of denitrification.

As evidenced from scattered Eh electrode measurements, conditions in the marshes studied were reducing except possibly in the upper few millimeters in some locations. The important bacterial activity occurring was anaerobic ammonification and the chief inorganic nitrogen form was ammonium. The amount of nitrate and nitrite was assumed negligible and not measured. It is likely, however, that small amounts of nitrate located in surface layers may have been undergoing denitrification in the anaerobic subsurface.

As mentioned previously, Rittenberg et al. (1955) studied nitrogen distribution in basin sediments and found that the organic nitrogen decrease with depth was not balanced by the inorganic nitrogen increase. Since nitrification was not occurring, it was concluded that this deficit was the result of ammonia lost to the overlying waters. It is known, however, that ammonium is capable of being held in the sediment in a non-exchangeable or fixed form (Bremner, 1965). It is possible that some of the apparent inorganic nitrogen loss was contained in this manner. The non-exchangeable ammonium in the marsh sediments was determined to see if an appreciable amount could be found.

It has been well established that soils have the capacity to fix ammonium in much the same way as potassium (Bremner, 1965). In general the amount of fixed ammonium in a particular soil depends on the amount of clay size particles and the types of clays present. Vermiculite, illite, and montmorillonite are all capable of fixing ammonium. Allison et al. (1953) have shown that illite and vermiculite can more easily fix ammonium than montmorillonite. For example, under moist conditions soil illite and vermiculite can fix substantial ammonium whereas montmorillonite cannot fix any. Stevenson and Dhariwal (1959) studied 17 different soil profiles and found that drainage, type of vegetation cover, and extent of the leaching of percolating water have little effect on the amount of fixed ammonium contained in the soils.

Although it is generally assumed that fixed ammonium is held in the lattice of silicate minerals, Bremner (1965) proposes that some of it may be in the form of complex ammonium phosphates or other types of ammonium salts. There is no evidence, however, to support this suggestion and no relationship between ammonium and phosphate was found from the present data.

Like other cations, ammonium is also capable of occupying the exchange sites of various silicate minerals. Of course, in a given soil, the amount of exchangeable ammonium present will depend on the abundance and type of clay minerals present. In most soils, however, exchangeable ammonium is one of the first cations to be leached out and replaced by other cations during lysimeter measurements (Bailey, 1968). The exchangeable ammonium in the marsh sediments was determined to see if substantial amounts existed.

Inorganic Phosphorus

Inorganic phosphorus in soils is almost always found as oxy-, fluro-, and hydroxy- phosphates of iron, aluminum, calcium, titanium, magnesium, and manganese (Bailey, 1968). Bailey (1968) gives a good review of the various mechanisms of phosphate fixation in soils.

Phosphate fixation is very dependent on the environment. The pH for instance, controls the form of phosphate resulting from fixation. Figure 2 shows the relationship of the different phosphate forms with pH.

In acid conditions iron and aluminum phosphates dominate while in alkaline environs, the predominant species is calcium phosphate or hydroxy phosphate. Hsu (1964) proposed that phosphorus can be fixed as iron or aluminum phosphate species above pH 7, not as the variscite or strengite type complexes, but as phosphates adsorbed on amorphous aluminum hydroxides and iron oxides or hydroxides. The activity of Al^{+3} (or Fe^{+3}) is limited by pH, being negligible at pH 5 or above. The activity of amorphous aluminum hydroxide and iron oxide have no such limitation and the activity can have any magnitude at any pH (Hsu, 1965).

Several workers (Williams and Saunders, 1956; Juo and Ellis, 1968; Frink, 1969) have shown that a correlation exists between grain size and phosphorus fixation. Juo and Ellis (1968) have found, in sub-surface soils, that aluminum and iron phosphates are always concentrated in the finer fraction while calcium phosphate is dominant in the coarse fraction. They concluded that calcium phosphate is of primary origin

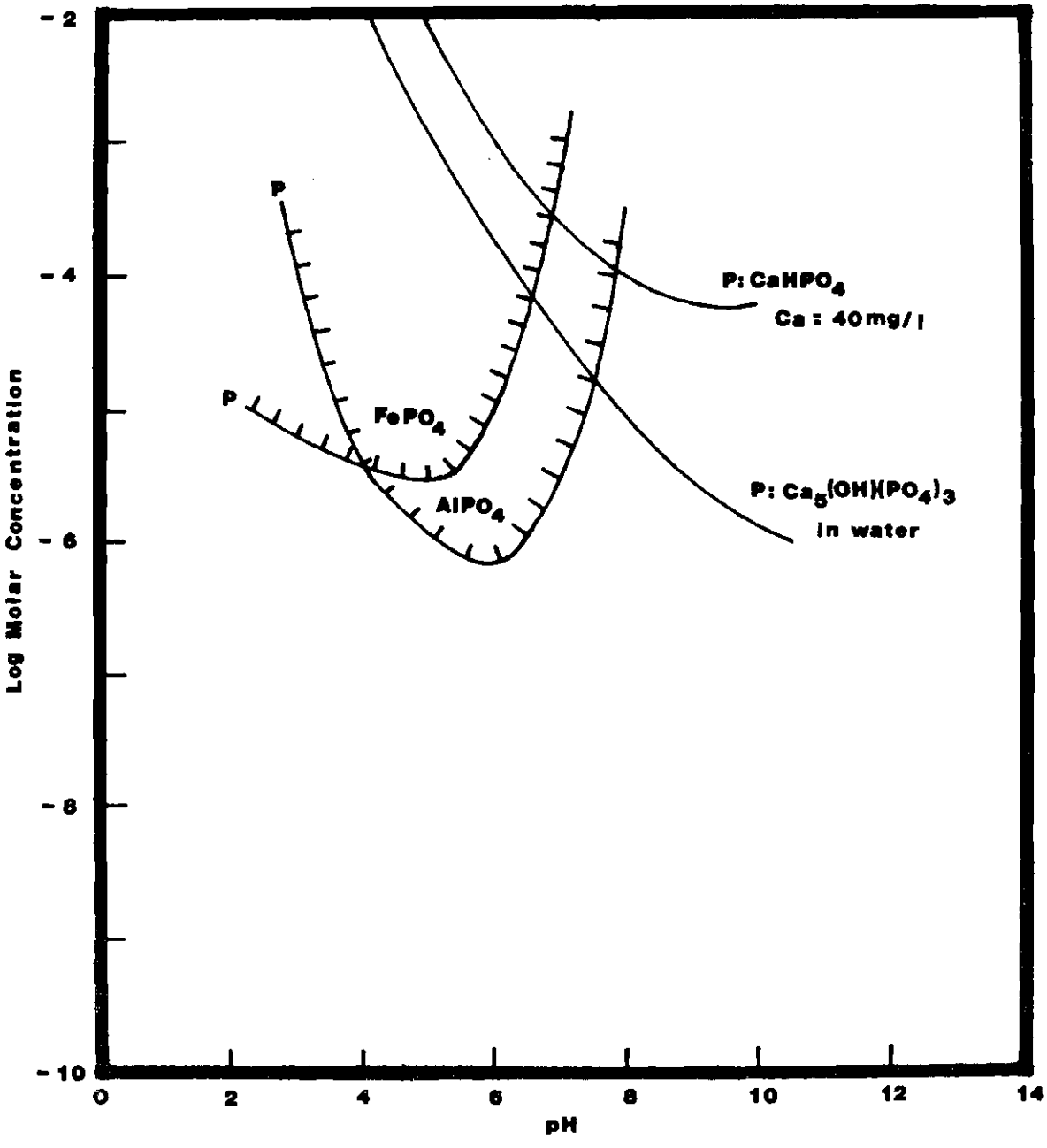

Figure 2. Effect of pH on Various Phosphate Forms
[From *Jour. AWWA*, 62:136.]

and that crystallinity, not grain size, is the controlling factor. Aluminum and iron phosphates, on the other hand, are of secondary origin. Frink (1969), studying eutrophic lake sediments, found that the calcium phosphate was concentrated in the sand size fraction and the aluminum and iron phosphates in the clay size fraction. He, however, does not believe that all the calcium phosphate is primary. Frink concludes that since there is a shift from aluminum and iron phosphate in acid soils to calcium phosphate in neutral soils, a chemical conversion is actually taking place and that all the calcium phosphate in the lake sediments is probably not of primary origin. The size sorting, he suggests, may simply result from an increase in crystallinity and particle size as the calcium phosphate is formed.

The action of organics in phosphate fixation has not been studied thoroughly but Harter (1969) considers organic matter very important in the initial bonding of phosphate in soils. That is, the phosphate is first bonded to anion exchange sites on organic matter and subsequently transformed to less soluble iron and aluminum phosphate. Harter further suggests that since organic matter is responsible for phosphorus adsorption, the sediment may act as both a sink and a reservoir. The sediment is continually enriched with phosphorus by adsorption and then by precipitation as Al and Fe-PO_4, it acts as a sink. If the phosphorus in the interstitial waters decreases, the sediment may release the phosphorus which is in the anion exchange sites and act as a reservoir. Since organic matter is abundant in the marshes, it is possible that this sink-reservoir type system is active in the sediments.

Pomeroy et al. (1965) studied the exchange of phosphate between bottom sediments and waters of Doboy Sound, Georgia, and found that a two-step ion exchange process takes place between the clay minerals and overlying water. The first step is the rapid initial sorption on the clay's surface and the second step is a secondary combination of phosphate into the crystal lattice of the clays. The second step occurs at a slower rate than the first. Pomeroy's work supports the theory that the sediment acts as a buffer on the phosphate content of the water and the buffering effect may be partly due to the organics associated with the clays as Harter suggests. It is this rather loosely-held surface phosphate that is returned to the waters if the phosphate concentration decreases below an equilibrium value. As in the estuaries, the phosphate concentration in the marshes' interstitial waters is likely to be buffered by the same process, involving clay minerals and associated organic matter.

The estuaries of coastal Georgia are enriched with inorganic phosphorus and the most important contributing factor is the large population of marsh grass, *Spartina alterniflora* (Pevear, 1966). Pevear (1966) reported inorganic phosphorus values in Georgia estuaries to range from 1-4 mg-atoms/m^3 while in nearby rivers and the ocean, it averages only 0.1 mg-atoms/m^3. It is obvious that the estuarine phosphorus content is due to high productivity within the estuaries and marshes and not from influx of river and ocean waters.

Noting the importance of the marshes in the overall phosphorus content of the estuaries, it was the purpose of this work to determine

what inorganic forms of phosphorus, such as Al-PO_4, Fe-PO_4, and Ca-PO_4, were being fixed by the marsh sediments and how the relative abundance of each was affected by environmental factors.

CHAPTER II

SAMPLING

Description of Location

The salt marshes (Hoyt et al. 1964) along the Georgia coast generally have surface sediments which are homogeneous gray to black silty clay and range in thickness from several centimeters along the margins to over two meters in the mid-marsh areas. Thin laminae of sand may be found in this layer. Beneath the silty clay surface, the material grades into laminated sands, silts and clays. The marshes usually have a heavy growth of marsh grasses and plants, primarily *Spartina alterniflora.*

Except for the very surface layer, the marshes are a reducing environment. In most locations, H_2S is noticeable at the surface. The sediments, on the average, as determined in this study, contain about 53.4 per cent water by weight and this interstitial water has average salinity of 22.6 parts per thousand and pH values ranging from about 5 to 8. The data for each sample are given in the Appendix. Salinity and pH values were obtained from the Skidaway Institute of Oceanography. The abundance of organic matter, particularly *Spartina alterniflora,* is probably the most important factor contributing to geochemical processes. It is known that marsh grass is a major source of inorganic phosphorus (Peavear, 1966) and recent studies (Hall et al., 1970) have shown that *Spartina* contains a higher percentage of amino acids than previous

evidence indicated. It is possible that these amino acids may be the major source of inorganic nitrogen in the estuaries.

Thirteen cores were taken during the months of July and August in various marshes around Skidaway Island, Georgia, and along the Little Ogeechee River and the south channel of the Savannah River (see Figure 3). The particular locations were generally chosen because of accessibility.

Coring Procedure

All cores were recovered by a piston corer modified from the design of Byrne and Kulm (1967). The core barrels were 6.3 cm diameter aluminum pipe and the piston was milled from a No. 14 rubber stopper. An eight-foot tripod, constructed from one-inch diameter steel pipe, was used as support for the corer. Each leg of the tripod had a large plyboard foot which facilitated the support's use in the marsh.

The cores were taken by hand and the depth of penetration and recovery depended on the location. The length of useable core ranged from 0.5 to 1.5 meters. The sediment was not extruded from the barrel, but the core was cut into 15 cm sections and a sample taken from each section.

Squeezing Procedure

The interstitial waters were removed from the sediment by a gas-operated squeezer modified from the design of Reeburgh (1967). The squeezer used had a sample chamber with a volume of approximately 1,120 cm^3 and the nitrogen pressure required ranged from 20 to 40 psi depending on the sample.

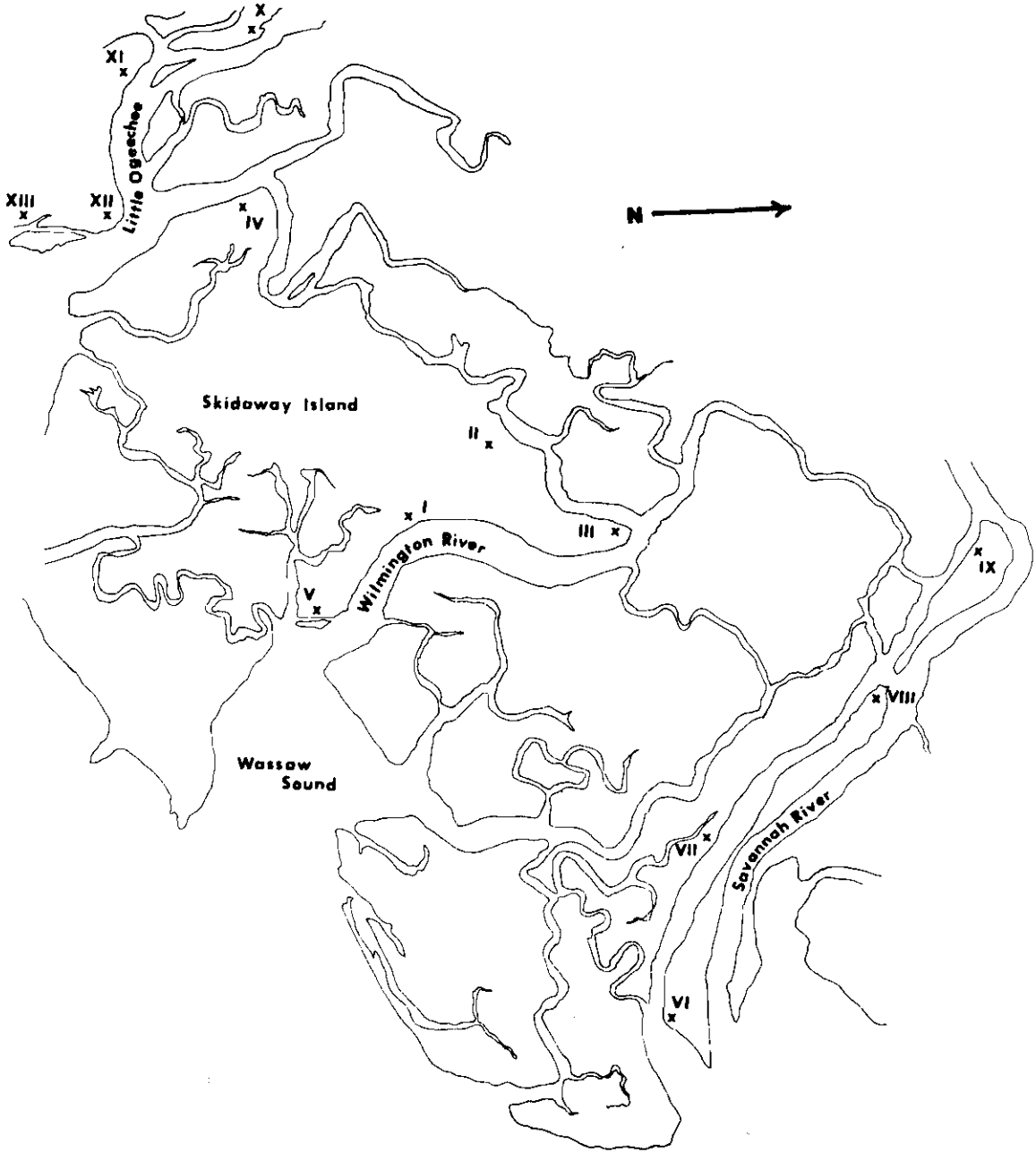

Figure 3. Location of Cores I-XIII

In operation, a rubber diaphragm, made from an auto inner tube, was inflated. The diaphragm then compressed the sediment. The pore water was forced out through a series of nylon mesh discs and finally through Whatman No. 40 filter paper. The flow rate obtained was 1-2 ml/min. Approximately 20 ml was collected for subsequent analysis.

CHAPTER III

ANALYTICAL PROCEDURES

Analysis of Interstitial Waters

Ammonium

Ammonium in the interstitial waters was determined immediately after squeezing. The pore water was filtered through a 0.45 μ, Type HA Millipore filter prior to analysis. The method used was a modification of the Conway microdiffusion technique (Conway and O'Malley, 1942). Sixty-eight mm diameter polypropylene diffusion dishes (Fisher Scientific, No. 8-764B), based on the Obrink modification (Obrink, 1955), were used. The size of the dish limits the amount of sample that can be used and thus the lower limit of ammonium that can be determined. In this case the maximum sample of 4 ml was used. One ppm NH_4^+ could be accurately detected with this procedure. When concentrations of less than 1 ppm were found, they were recorded as trace amounts of NH_4^+.

The Obrink type diffusion dish has three chambers and is covered by a lid which makes a liquid seal with 40 per cent K_2CO_3 in the outer chamber. One milliliter of a boric acid indicator (McDonnell and Murphy, 1952) solution is placed in the inner chamber and 4 ml of sample is carefully pipetted into the middle chamber. Finally approximately one milliliter of the 40 per cent K_2CO_3 solution is rapidly added to the sample and the dish is immediately sealed. The dish is allowed to stand for a diffusion time of three hours, and then the contents of the inner

chamber are titrated with 0.005 NHCl. It should be noted that several diffusion times were tried in order to determine an optimum. Diffusion was essentially complete after three hours. A series of standards containing 5, 10, 15, and 20 ppm ammonium (NH_4Cl) were carried through the analysis. They gave a linear calibration curve in this concentration range.

This method is quick and easily reproducible since it involves only one accurate pipet addition, that being the 4 ml sample. McDonnell and Murphy (1952) suggest the same general procedure for ammonium determination but use 40 per cent NaOH instead of the potassium carbonate solution.

Phosphate

Freshly recovered pore waters were frozen until analyzed for phosphate. In every case, the phosphate was determined within 12 hours of recovery.

The spectrophotometric method proposed by Stephens (1963) was used, although an isobutanol extraction was not made. Standards of 0, 2, 5, 10 ppm phosphate (KH_2PO_4) were run with samples and the sample phosphate determined from the calibration curve.

A 2 ml aliquot of sample was transferred to a plastic beaker and 0.2 ml of mixed reagent was added with a 0.1 ml Grunbaum pipet. After ten minutes the color was measured at 882 NM on a Spectronic 20 using a flow cell apparatus. When samples ran above 10 ppm, they were diluted by one-half by mixing 2 ml sample with 2 ml distilled water. A 20 ppm phosphate standard and a blank were diluted similarly and run as a reference.

Analysis of Sediment

Sample Storage

Immediately after cutting from core, approximately 100 grams of each sample were frozen. Just prior to analysis they were thawed and dried at 110°C. Moisture content was found and the dried samples were used for exchangeable and nonexchangeable ammonium and phosphate fraction determinations.

It is realized that for optimum result, sediments should be analyzed for exchangeable or fixed ammonium immediately after sampling. The inorganic nitrogen forms can undergo rapid changes due to bacterial processes and many workers have examined the problem of sample storage. Gasser (1958) found no change in ammonium content when soils were stored at -10°C for 32 days, but Allen and Grimshaw (1962) did find a change in exchangeable ammonium in soils stored at -15°C (amount of change not given in referenced work). It would seem that freezing is not a completely satisfactory method of preserving samples, but for lack of a more defined technique, the method was adopted here. There is also controversy over whether drying affects the inorganic nitrogen content of sediments. There is some evidence that drying results in an increase in exchangeable ammonium (Allen and Grimshaw, 1962) while Stevenson et al. (1967) found no significant change in the ammonium content of a variety of soils containing illite, montmorillonite, and amorphous material. Piper (1944) suggested that samples which were to be analyzed for inorganic nitrogen should be dried rapidly in an oven at 55°C. This method has been adopted by many workers. In the marsh sediments

collected, where the water content ranged from 50 to 60 per cent, it was necessary to dry the samples prior to analysis. It is unfortunate that sample storage should be of such concern, but when dealing with inorganic nitrogen in sediments, storage is important and any storage method will be, in some respects, unsatisfactory. It is realized, therefore, that changes in the ammonium content of the collected samples may have taken place prior to analysis and the magnitude of any changes is unknown. All samples, however, were treated equally and any relative differences in ammonium content should remain, assuming of course that the differences remained above the detection limit.

Exchangeable Ammonium

Although there is no single accepted definition of exchangeable ammonium in soils, most workers have found it convenient to define it as that ammonium which is extractable by 1N HCl at laboratory temperatures (Bremner, 1965). This definition is assumed in this work.

For the extraction, approximately 10 gm of dried sediment, accurately known, was hand ground. Heavy grinding was avoided since it may lead to the release of fixed ammonium (McDonnell et al., 1959). The sample was placed in a 250 ml centrifuge bottle to which was added 100 ml of 1NHCl. It is noted by Bremner (1965) that 10 ml of extractant per gram of soil is sufficient to recover any exchangeable ammonium. The bottle was placed on a shaker table (250 cycles/min) for one hour after which the contents were centrifuged and the clear extract saved for analysis.

The ammonium in the extract was determined by steam distillation with MgO (Bremner, 1965). The distillation apparatus used is described by Bremner (1965, p.1196). One milliliter of boric acid indicator (McDonnell and Murphy, 1952) was added to a 50 ml graduated plastic beaker which was placed under the condenser of the apparatus. Approximately 0.2 gm of heavy MgO (Fisher Scientific, No. M-50) was added to a 100 ml Kjeldahl flask and then 20 ml of the extract was transferred by pipet to the flask, care being taken to wash any MgO off the walls. The flask was attached to the apparatus and distillation begun. When the distillate reached 10 ml in the beaker, the distillation was stopped. The ammonium in the distillate was determined by titrating with 0.005N H_2SO_4 with a microburette. A blank and standards containing 2 and 6 ppm ammonium were also distilled and analyzed. The sample concentrations were determined from the resulting calibration curve.

Nonexchangeable Ammonium

In the determination of nonexchangeable or fixed ammonium, the sample is generally treated with hydrofluoric acid solution to decompose the silicate minerals. To be completely satisfactory, it is desirable that the acid solution release the fixed ammonium without decomposing organic forms of nitrogen to ammonium-nitrogen. Several solutions of varying acid strengths have been tested. Bremner (1965) proposed shaking the soil for 24 hours in a solution of 1N HF:1N HC_1. Evidence, however, indicates that better results can be achieved by use of a solution of 2.5N HF-0.1N HCl (Stevenson et al., 1967). It was found that increasing the HF strength at the expense of the stronger HCl would reduce the

chance of the degradation of organic matter. Stevenson et al. (1967) further showed that amino acids and sugars, in the presence of soil materials, were stable in the 2.5N HF-0.1N HCl solution. It is understood that some organic -N which is closely associated with clay minerals may be released when the clay is destroyed with any HF solution (Freney, 1964; Stevenson, 1959). However, in the work herein, any ammonium extracted by 2.5N HF-0.1N HCl which is not accounted for as exchangeable will be considered fixed ammonium.

Stevenson et al. (1967) studied the effects of grinding on the extraction of fixed ammonium and found that best results were obtained when the samples were ground so that approximately 80 per cent passed through a 300-mesh sieve. This procedure was adopted here and the proper sample grain size was obtained after the dry samples were ground in a Spex mixermill for 30 minutes. For the extraction, one gram of this ground sample was placed in a 100 ml centrifuge tube and 20 ml of 2.5N HF-0.1N HCl added. The sample was shaken for 24 hours on a shaker table (250 cycles/min) after which the contents were centrifuged and the clear extract saved for analysis.

Steam distillation was also used to determine the ammonium in this extract. The method used is essentially the one outlined by Bremner (1965) although the sample size was reduced. Seven milliliters of 10 NKOH were placed in a 100 ml Kjeldahl flask which was marked to indicate 30 ml. A 10 ml aliquot of sample was added using a plastic pipet and the contents made up to 30 ml with deionized water. The flask was attached to the distillation apparatus and the distillate

collected in a plastic beaker containing one milliliter of the boric acid indicator. When 10 ml had been collected, it was titrated with 0.005N H_2SO_4 to determine ammonium content. Standards of 2, 6, and 10 ppm ammonium were analyzed to obtain a calibration curve.

Cation Exchange Capacity

When comparing the exchangeable or nonexchangeable ammonium content in a variety of samples, it is necessary to take into account the relative clay percentage of each sample. Since a particle size fractionation was not made, the cation exchange capacity was determined. In a group of similar samples, the cation exchange capacity yields a measure of the relative differences in clay content.

In the determination of cation exchange capacity a known weight (about 5 gm) of bulk sediment sample was washed two times in deionized water and then two times in $SrCl_2$ at pH 7. During each wash the sediment was ultrasonically dispersed in the agent and centrifuged for recovery. Following this the sediment was rinsed in deionized water until less than 1 ppm strontium (by atomic absorption) was found in water from last rinse. Finally the sediment was washed three times in about 25 ml of 0.5M $BaCl_2$ at pH 7. The supernatant $BaCl_2$ was saved and made up to 100 ml in a volumetric flask. This solution was analyzed by atomic absorption spectrophotometry for the concentration of strontium. From the strontium concentration, a calculation of the total cation exchange capacity in meq/100 gm was made. The sediment's dry weight, determined on a separate sample, was used.

In order to determine if parameters other than clay content affected the concentrations of exchangeable and nonexchangeable ammonium, it was necessary to normalize each sample in a core with respect to cation exchange capacity. This was accomplished by dividing the ammonium concentration of a sample by the sample's cation exchange capacity. Because the resulting number was very small, it was multiplied by the average cation exchange capacity of all the samples.

Phosphate Fractions

The concentrations of the three important phosphate species, aluminum, iron, and calcium phosphate, were determined for each of the marsh samples. Phosphates which are insoluble in both alkali and acid were not determined. The nature of these phosphate species has been only partly characterized (Bauwin and Tyner, 1954). The method used for the fractionation is that of Chang and Jackson (1957) which involves the stepwise extraction of the three forms. Aluminum phosphate is extracted by ammonium flouride, iron phosphate by sodium hydroxide, and calcium phosphate by sulfuric acid. For convenience, an overall reduction in sample and reagent size of one half, as suggested by B. W. Nelson in an unpublished study, was made.

The samples were ground in a Spex mixer-mill for 30 minutes prior to extraction. After this time about 80 per cent of the sample passed through 300-mesh sieve. The phosphate concentration in each extraction was determined on a Gilford spectrophotometer. Standards containing 0, 2.5, and 5 ppm phosphorus were analyzed for a calibration curve.

CHAPTER IV

RESULTS AND DISCUSSION

Interstitial Waters

Ammonium

Ammonium concentrations in the interstitial waters varied considerably with location. Concentrations ranged from less than 1 ppm to 20 ppm where the 20 ppm is roughly 500 times as great as the maximum reported for sea water (Rittenberg et al., 1955). In cores where substantial ammonium occurred, the average concentration was about 8 ppm. All data values are given in the Appendix.

Of the four cores taken from the Savannah River area, cores VI and VIII showed as much as 16.8 ppm ammonium in the interstitial waters while cores VII and IX had only trace amounts. The reason for this is not clear although cores VII and IX were taken in more open and sparsely vegetated areas than cores VI and VIII. In fact, marsh grass in particular was sparse in all the sampling areas along the south channel of the Savannah River as compared to the other coring sites. In the Ogeechee River area the marsh grass was especially thick and only the short core XII failed to show substantial amounts of ammonium. The other five cores in this area contained varying concentrations of interstitial ammonium with the maximum concentration of 20 ppm occurring in core V.

In almost every case (core VI was a noted exception) there was a tendency for the ammonium concentrations to increase with depth. Figures 4 and 5 show this relationship for several of the longer cores. Rittenberg et al. (1955) found this same trend in marine cores and concluded that bacterial action was important at least to the depth of their cores which averaged about 400 cm. This same conclusion can be reached for these marsh cores.

It was thought, due to the heavily populated areas along the Savannah River, that the interstitial ammonium concentrations in the marsh cores might be influenced by the inflow of domestic wastes. Domestic wastewater, from primary and low-rate secondary treatment processes, contains from 18 to 28 ppm nitrogen of which the predominant species is ammonium nitrogen (McCarty, 1970). No such influence was obvious from this study, however, since cores from the less populated Ogeechee River area contained as high or higher ammonium concentrations than those from the Savannah River area.

Another possible source of nitrogen to the marshes could be agriculture drainage waters which may contain from 1 to 100 ppm nitrogen, mostly in the form of nitrate (McCarty, 1970). Nitrate, brought in by the rivers, would eventually undergo reduction to ammonium in the marshes. In order to establish the actual effect of agricultural drainage on the marshes, it would be necessary to have a yearly sampling program. Since agriculture is common along the Ogeechee River, it is possible that agricultural drainage may contribute to the relatively high ammonium concentrations found in the Ogeechee cores.

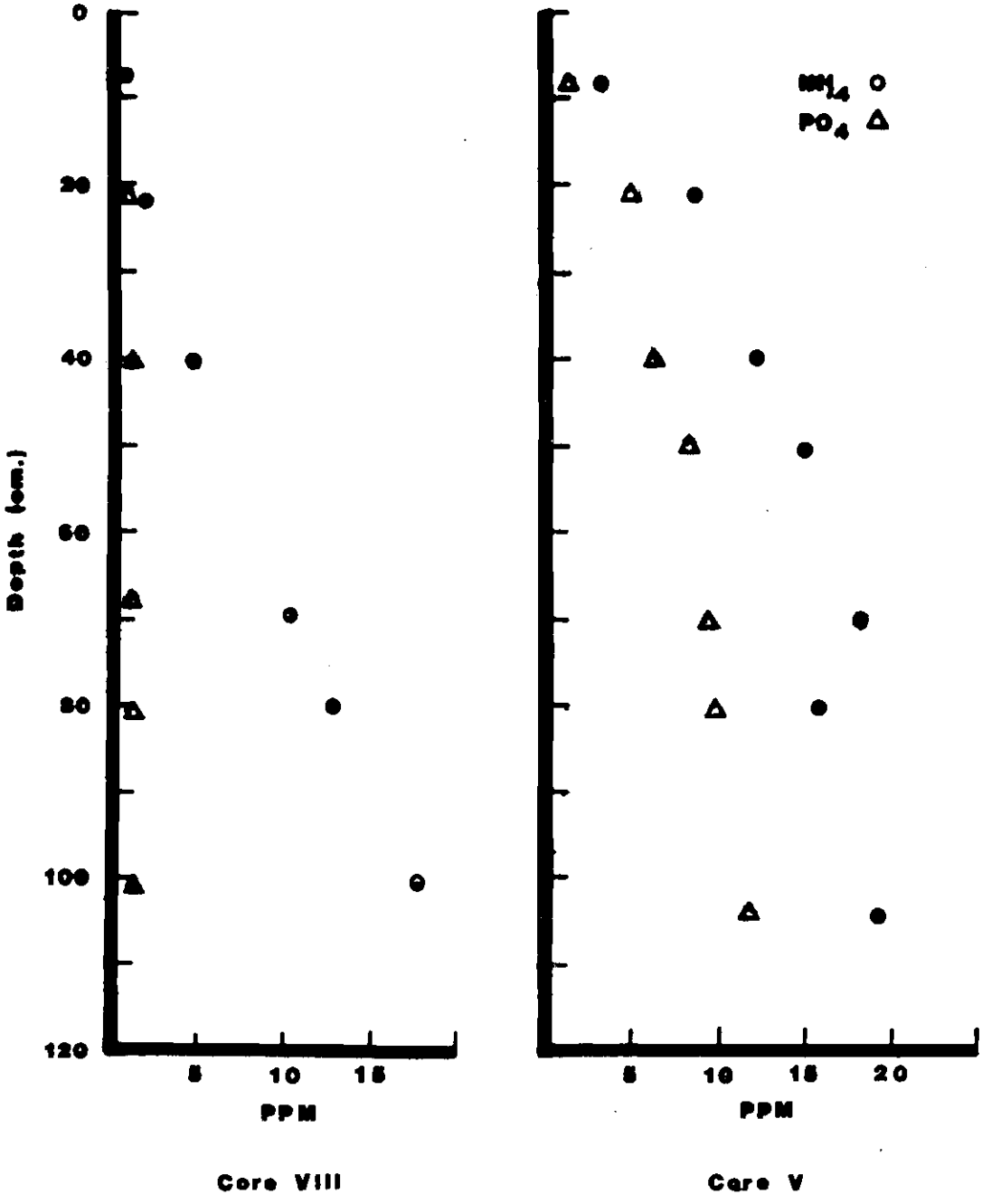

Figure 4. Ammonium and Phosphate Concentration of Interstitial Waters from Cores V and VIII

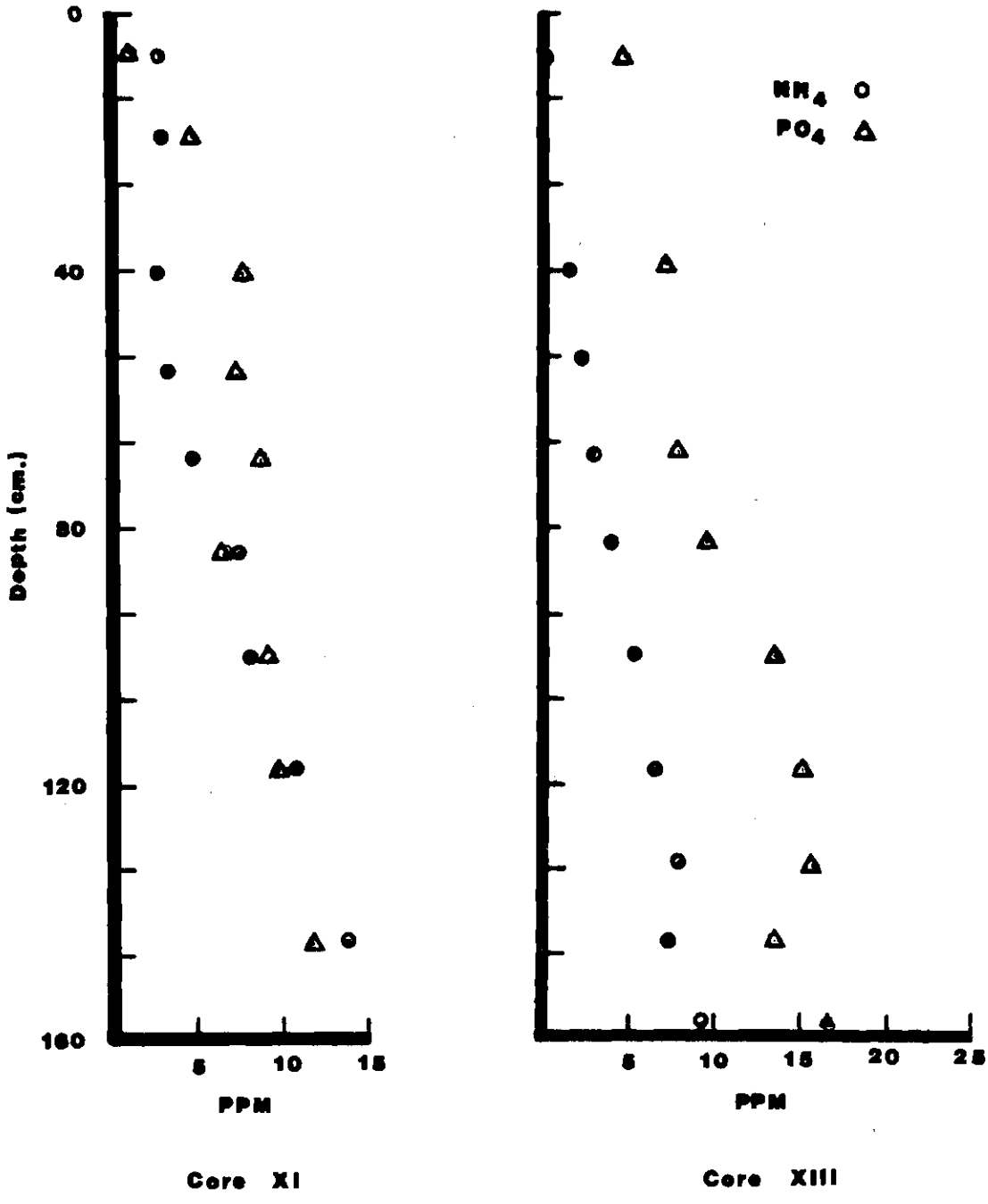

Figure 5. Ammonium and Phosphate Concentration of Interstitial Waters from Cores XI and XIII

A third possible source of nitrogen is the clay minerals being carried by the rivers. As previously mentioned, the clays can take up ammonium in exchangeable and nonexchangeable sites while in ammonium rich environments. When the clays are deposited in the marshes, all of the exchangeable and possibly a fraction of the nonexchangeable ammonium is available to enrich the interstitial waters. The ammonium associated with the clays will be discussed later.

Although domestic waste, agricultural drainage, and clay minerals may act as outside sources of nitrogen, it is believed that the primary nitrogen contributor is found within the marshes. Hall et al. (1970) have shown that *Spartina alterniflora*, which is extremely abundant in the Georgia marshes, contains a relatively high percentage of amino acids. The bacterial degradation of these acids is probably the most important source of nitrogen in the marshes.

In light of this, it seems reasonable that some of the cores along the Savannah River would contain less amonium than those along the Ogeechee River. At each sampling site in the Savannah area, the *Spartina* was sparse. In contrast the Ogeechee core sites were all in areas of extremely thick *Spartina* growth. The difference in *Spartina* availability could account for the variations in ammonium concentrations. It is believed that the presence of organic nitrogen from the decay of *Spartina* is by far the major source of the interstitial ammonium in the marsh cores.

Phosphate

The concentration of phosphates in the interstitial waters varied considerably with the core location. Concentrations ranging from trace to 16.5 ppm were found. The phosphate concentrations in the Savannah River cores were generally much lower than the others. The Ogeechee River area cores contained the highest phosphate concentrations.

As in the case of ammonium, the primary source of phosphates is the organic phosphorus derived from the marsh grass, *Spartina*. The contribution of phosphates from outside sources is small. As mentioned earlier, the rivers along the Georgia coast are very low in phosphates, 0.1 mg-atoms/m^3, as compared to the 1 to 4 mg-atoms/m^3 found in the estuaries and the difference has been related to the high production of *Spartina* in the marshes (Pevear, 1966). The heavier *Spartina* growth in the Ogeechee coring sites probably accounts for the fact that higher phosphate concentrations were found in the Ogeechee cores than in the Savannah cores.

Phosphate concentrations are also similar to ammonium concentrations in that they tend to increase with depth. Figures 4 and 5 show this relationship for some of the longer cores in the present study. Rittenberg et al. (1955) also found this same trend in their marine basin cores.

Exchangeable and Nonexchangeable Ammonium

Low concentrations of exchangeable ammonium were found in the marsh sediments. Values ranged from around 0.01 meq to 0.3 meq per

100 grams of bulk sediment. The concentrations were quite varied and showed no distinct relationship with depth.

Nonexchangeable (fixed) ammonium was found in varying concentrations ranging from 0.2 to 1.2 meq per 100 grams of bulk sediment. Again, no relationship of fixed ammonium concentration with depth was seen. The fixed ammonium was always present in greater concentrations than the exchangeable form. On the average it was five times greater. Figure 6 shows exchangeable and fixed ammonium (normalized) for some of the longer cores.

It is noted that in some of the cores, where only traces of ammonium were found in the interstitial waters, ammonium in the sediment was still present in rather large amounts (e.g. cores VII and XII). Although the presence of the exchangeable ammonium in these cases is difficult to explain, it is possible that the fixed ammonium is detrital in that it was taken up by the clay minerals prior to deposition in the marshes.

As noted previously, Rittenberg et al. (1955) found that a decrease in organic nitrogen with depth was not balanced by an increase in inorganic nitrogen (mostly NH_3-N) in marine basin cores. The interpretation was that some of the ammonia nitrogen was being lost to the overlying waters. They further calculated that about two-thirds of the ammonia nitrogen formed from the organic nitrogen remained in the interstitial waters while one-third was lost. It is possible, although certainly not conclusive, that in light of the present work some of this ammonia nitrogen is not lost to overlying waters but is fixed by clay

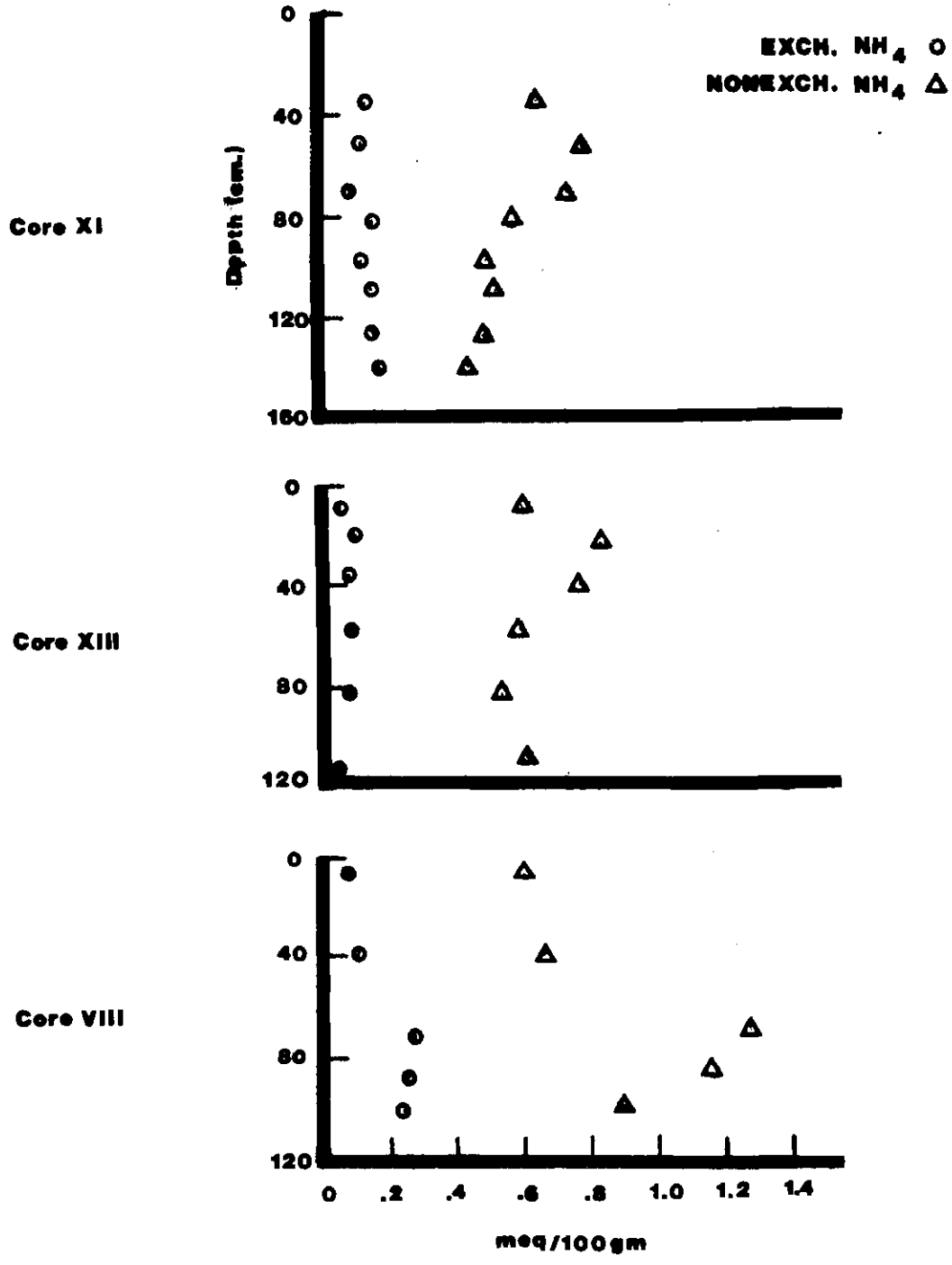

Figure 6. Exchangeable and Nonexchangeable Ammonium vs. Depth

minerals in the sediments. If one assumes 200 cm^3 of wet sediment, a dry density of 2.5, and the average values found in this study (50 per cent water content, 8 ppm interstitial ammonium, 1 meq/100 gm fixed ammonium), a calculation can be made which shows that the sediment contains 0.8 mg ammonium in the interstitial water and 45 mg fixed ammonium. The marsh sediments studied are therefore more than capable of fixing the one-third ammonium which Rittenberg et al. (1955) considered lost. Although no increase in fixed ammonium with depth was found in the present study, if longer cores could have been obtained, such a trend may have been seen.

As expected, the controlling factor in the amount of exchangeable and nonexchangeable ammonium in the sediments is the percentage of clay present. Figure 7 shows the concentrations of exchangeable and nonexchangeable forms (not normalized for CEC) as a function of cation exchange capacity.

Phosphate Fractions

The concentration of the Al-PO_4 fraction was fairly constant in all cores, averaging about 2.80 moles/gm. The $FePO_4$, however, was more varied and averaged 2.02 for the Ogeechee area, 1.48 for the cores around Skidaway Island, and noticeably higher, 3.40, for the Savannah River area. Average amounts of Ca-PO_4 found were 5.94, 5.17 and 7.69 moles/gm for the Ogeechee, Savannah, and Skidaway cores respectively. Ca-PO_4 averages are misleading in the fact that very high Ca-PO_4 fractions are seen only in the most seaware cores, i.e. VI, V, XII, XIII.

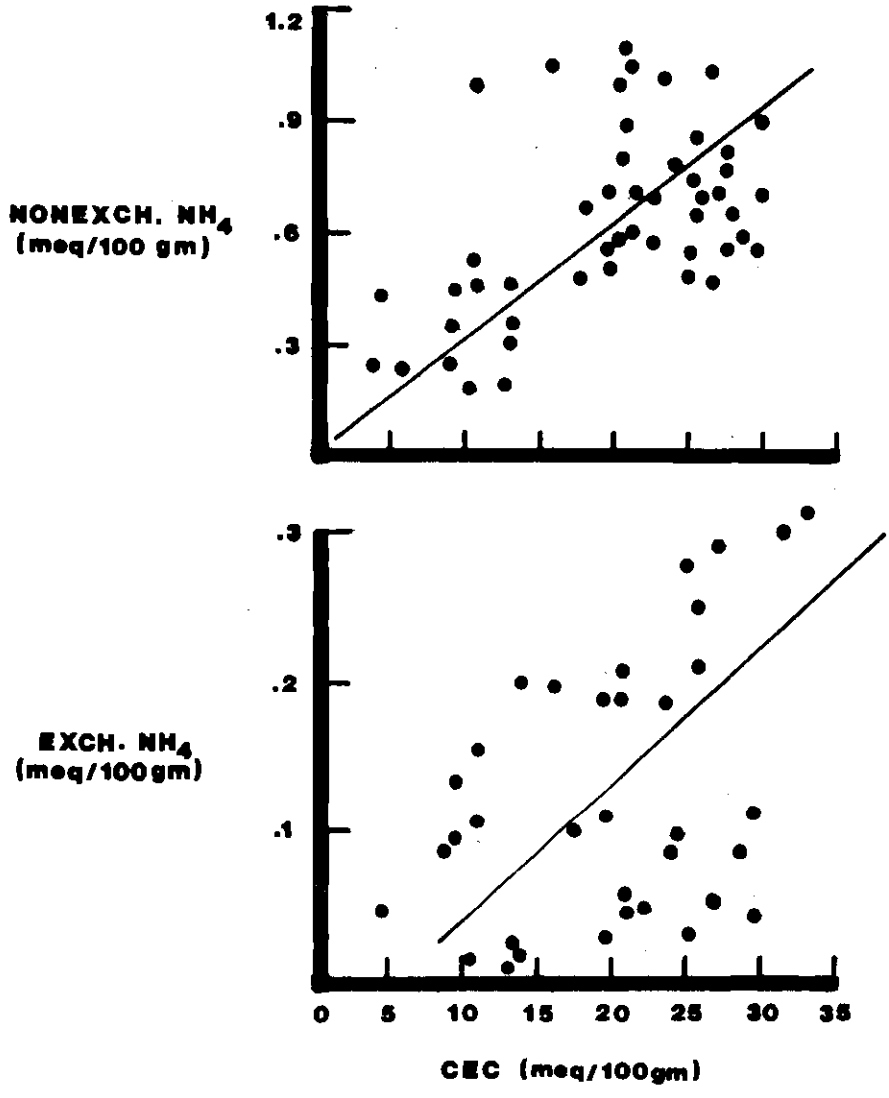

Figure 7. Exchangeable and Nonexchangeable Ammonium vs. Cation Exchange Capacity

Salinity values, furnished by the Skidaway Institute of Oceanography, were available for cores in the Savannah and Ogeechee River areas and a very distinct relationship exists between salinity and the concentration of the various phosphate fractions. See Figure 8. In the more dilute and acidic (pH 6-7) waters, Al-PO_4 and Fe-PO_4 are the most dominant forms. However, as salinity and pH increases, the Ca-PO_4 becomes by far the most important species. It is noted that the curves in Figure 8 not only reflect lateral changes in salinity but also changes of interstitital water salinity with depth.

There have been several studies (Frink, 1969; William and Saunders, 1956) in which the phosphate fractions have been related to grain size. In all the studies, it was found that Ca-PO_4 was highest in the sandy soils while Al-PO_4 and Fe-PO_4 were always highest in the finer soils.

Since CEC is a measure of the amount of clay size particles in a sediment, a relationship should exist between the CEC and the phosphate fractions. As can be seen in Figure 9, such a relationship does exist for the marsh sediments studied. The Al-PO_4 and Fe-PO_4 increases with increasing CEC and thus increases as the percentage of clay size particles becomes larger. Ca-PO_4, on the other hand, decreases while increasing CEC and is thus more abundant in the more sandy sediments. In light of similar results on soil studies, Williams and Saunders (1956) and Juo and Ellis (1968) concluded that the Ca-PO_4 was likely of primary origin. It is difficult to reach such a decision when dealing with marsh sediments because the effect of salinity on the relative

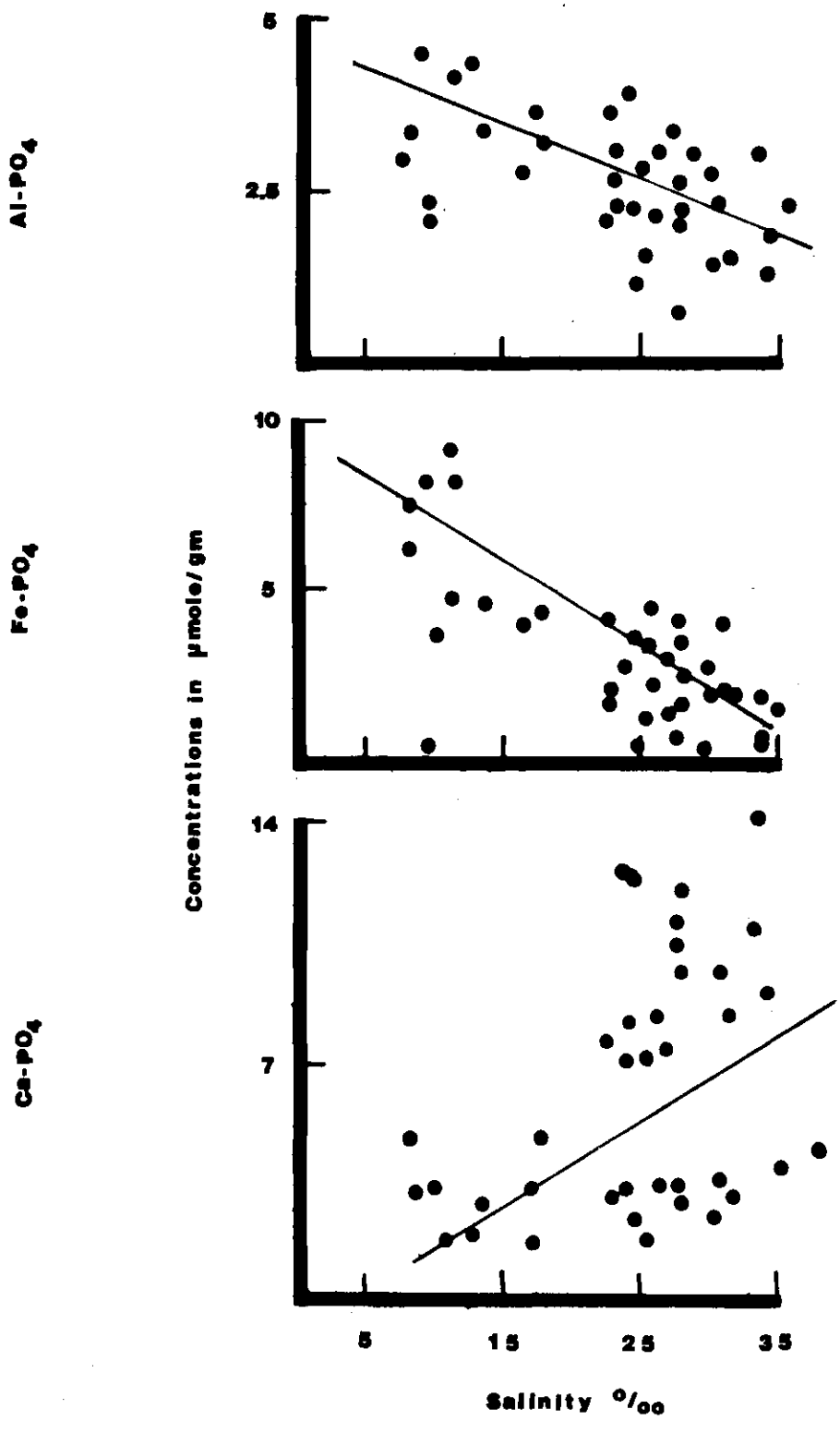

Figure 8. Concentration of Phosphate Fractions vs. Salinity

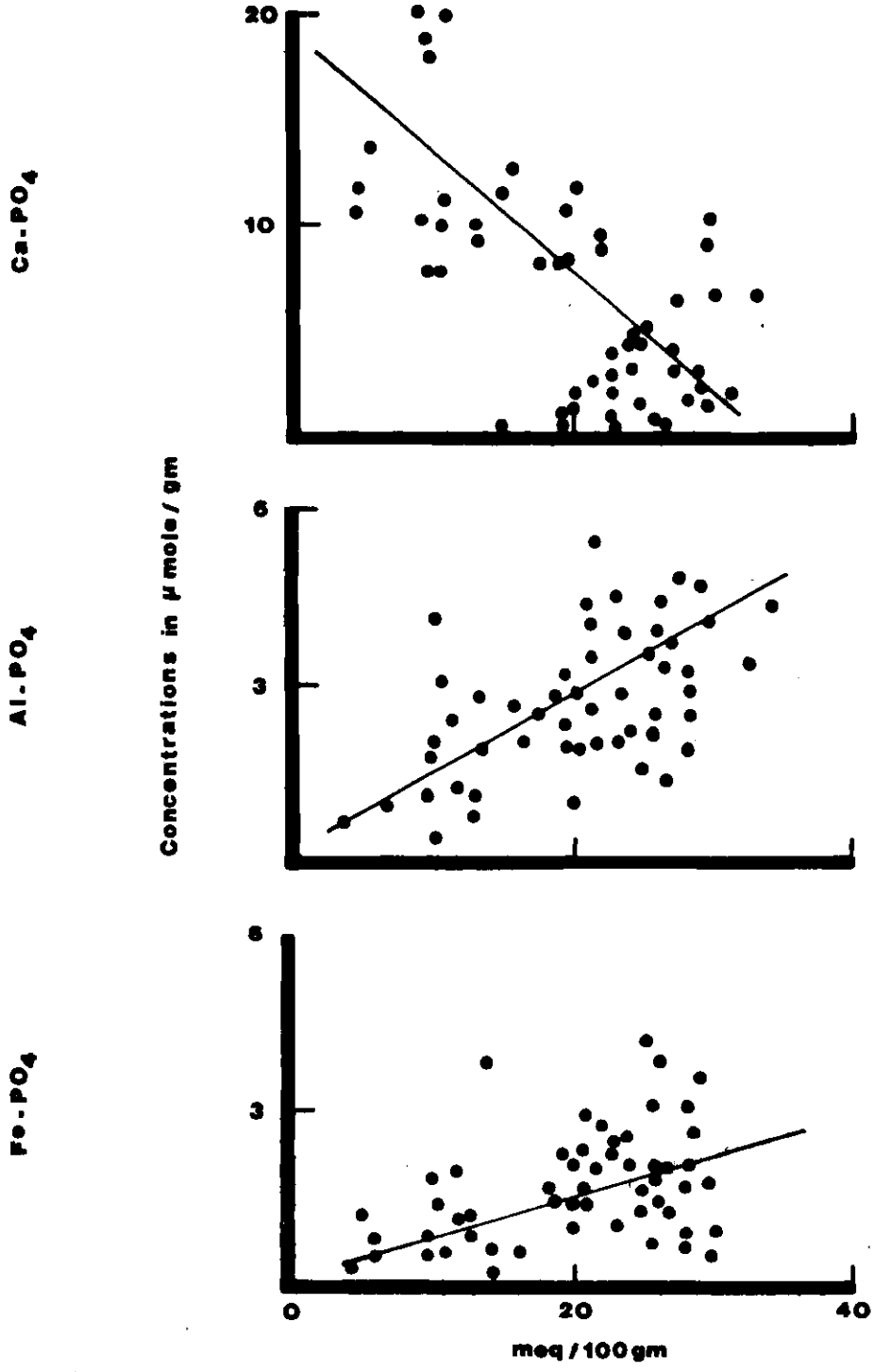

Figure 9. Concentration of Phosphate Fractions vs. Cation Exchange Capacity

amounts of phosphate fractions must be considered. The higher salinities are found for the interstitial waters of the coarser sediments. The chemical conversion from Al-PO_4 and Fe-PO_4 to Ca-PO_4, as previously discussed, is no doubt important (Frink, 1969). It is probably true that when dealing with continental to marine lateral variations, both grain size and salinity are good indicators that either Al-PO_4 and Fe-PO_4 or Ca-PO_4 are the dominant phosphate fractions present. It is difficult to determine if one indicator is more important than the other because in general both grain size and salinity increase as one moves seaward.

Nelson (1967) has suggested the use of phosphate fractions in estimating paleosalinities. He determined the Al, Fe and Ca-PO_4 fractions for a number of bottom sediments, most from the Rappahannock River and Chesapeake Bay and from this he plotted the ratio Ca-PO_4 to Ca-PO_4 + Fe-PO_4 (Ca-Fract) versus salinity. The result could be estimated by a straight line curve of the following form:

$$\text{Ca-Fract} = 0.09 + 0.026 \times \text{salinity}$$

In the present work, the same factor (Ca-Fract) was plotted versus salinity and the results are shown in Figure 10. Although there is considerable scatter, if one were to fit a best line, it would have the following equation:

$$\text{Ca-Fract} = 0.1 + 0.023 \times \text{salinity}$$

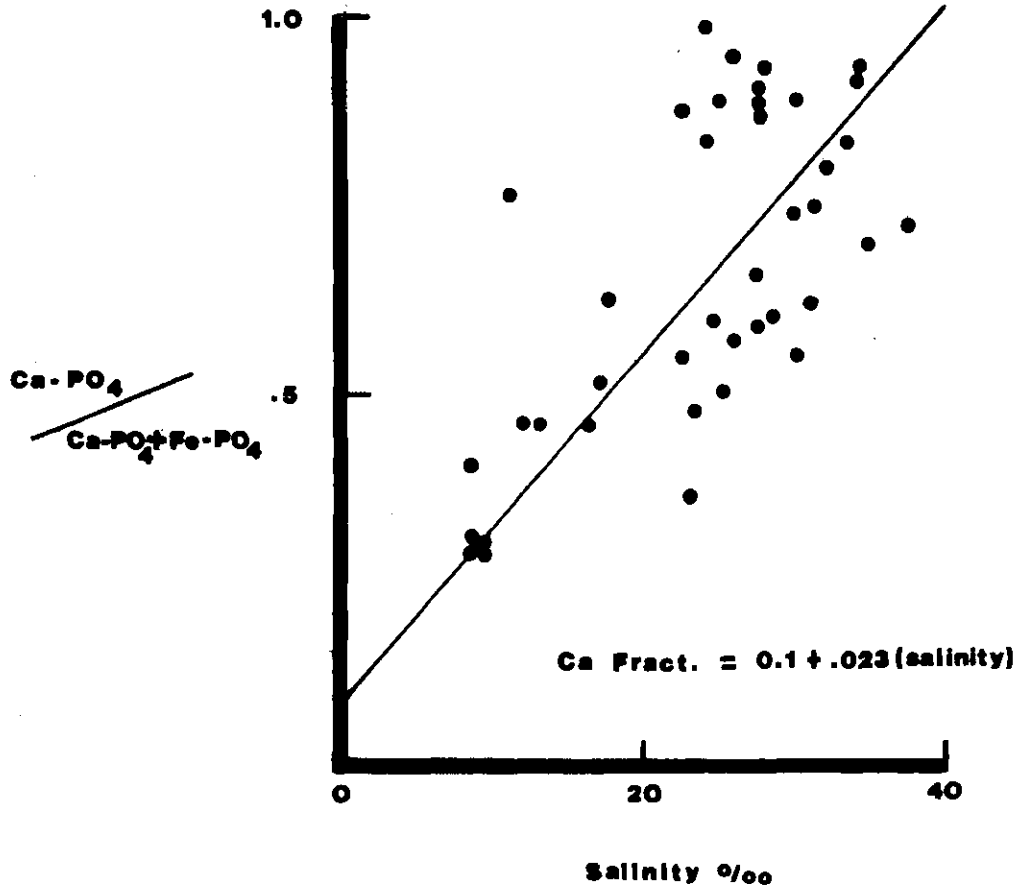

Figure 10. Calcium Phosphate Fraction vs. Salinity

which is surprisingly close to Nelson's equation. It should be remembered that here changes in salinity with depth are taken into account, whereas Nelson's data only reflected lateral changes in bottom salinity. This would likely contribute to the high scatter in data points. Also, unlike Nelson's study area where only the Ca and Fe fractions were important, the Al fraction in the marsh sediments was often more abundant than the Fe fraction. This probably reflects differences in the geology and soil properties of the drainage areas.

It should be noted that Nelson's method for estimating paleosalinities is dependent on two important assumptions: first, the $Ca\text{-}PO_4$ must be entirely of inorganic origin (Guber, 1969) and second, none of the $Ca\text{-}PO_4$ can be detrital (Muller, 1969).

CHAPTER V

CONCLUSIONS

1. The concentration of ammonium in the interstitial waters of the marsh cores ranged from trace amounts to 20 ppm and was highest in areas of thick *Spartina* growth.

2. The concentration of phosphate in the interstitial waters ranged from trace amounts to 16.5 ppm and was also highest in areas of thick *Spartina* growth.

3. The concentrations of interstitial ammonium and phosphate increased with depth in core.

4. The marsh sediments contained ammonium in both exchangeable and nonexchangeable positions. The nonexchangeable or fixed ammonium was always present in greater amounts than the exchangeable ammonium.

5. The amount of exchangeable and fixed ammonium present increased with the cation exchange capacity of the sediment.

6. The aluminum and iron phosphate fractions in the marsh sediments decreased with increasing salinity and increasing grain size.

7. The calcium phosphate fraction increased with increasing salinity and increasing grain size.

CHAPTER VI

RECOMMENDATIONS

In any study dealing with the analysis of nitrogen forms, sample deterioration is always a concern. Naturally it is desirable to make the analysis immediately after obtaining the core. Of course this is seldom possible and in the present study as much as eight hours elapsed from sampling in the field to analyzing in the laboratory. It would be helpful in future study to set up a small laboratory on a boat near the sampling location so that interstitial ammonium analysis could be begun soon after core recovery.

It was found that taking cores in the marshes was a very time-consuming and unpleasant task. There was a great need for a vehicle which could travel over the marshes and from which a core could be taken. Having to carry equipment over marshes on foot can be very discouraging to future research in these areas. Of course the coring procedure itself was not completely satisfactory and improvements should be made. For example, some type of core catcher device would be very helpful.

A natural follow-up to the present study would be research in which both inorganic and organic forms of nitrogen and phosphorus are determined. This is a necessity in obtaining a true picture of the marshes' role in the nitrogen and phosphorus cycles. It would also give

a clearer picture regarding the importance of the fixation of ammonium by the clay minerals.

APPENDIX

Table 1. Field and Analytical Data from Core I

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	50.3	9.3	9.3	.05	.04	.73	.62	24.2
23	54.3	12.1	9.8	.21	.16	.90	.67	28.1
38	53.3	14.4	7.6	.44	.33	.71	.53	27.7

Depth in Cm	PH	Phosphate Fractions in moles/gram		
		$Al\text{-}PO_4$	$Fe\text{-}PO_4$	$Ca\text{-}PO_4$
3	5.3	3.61	1.46	2.83
2	6.9	3.85	1.78	4.01
1	7.1	4.41	1.16	2.84

Table 2. Field and Analytical Data from Core II

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	-	Trace	.1	.10	.08	.77	.66	24.2
23	-	Trace	3.3	.07	.05	.54	.40	27.6
38	-	.5	3.8	.02	.03	.28	.48	12.1
53	-	1.2	1.8	.02	.03	.18	.30	12.6

Depth in CM	PH	Phosphate Fractions in moles/gram		
		$Al-PO_4$	$Fe-PO_4$	$Ca-PO_4$
8	5.9	2.21	3.89	2.52
23	6.4	2.92	1.75	0.79
38	6.8	1.17	.39	0.31
53	6.8	1.47	.63	0.63

Table 3. Field and Analytical Data from Core III

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	57.8	4.3	4.7	.22	.22	1.10	1.10	20.6
23	57.9	6.0	4.1	.18	.18	.91	.94	20.1
38	55.6	8.5	5.3	.18	.16	.67	.59	23.5
53	51.3	7.7	7.1	.10	.12	.62	.73	17.6
68	33.6	10.0	6.8	.11	.23	.36	.76	9.8
83	35.2	13.5	7.1	.10	.12	.45	.54	17.4
98	33.0	14.2	8.7	.20	.20	-	-	9.5

Depth in CM	PH	Phosphate Fractions in moles/gram		
		$Al-PO_4$	$Fe-PO_4$	$Ca-PO_4$
8	6.8	5.15	2.52	3.47
23	6.8	4.24	2.03	2.97
38	6.9	3.76	1.94	3.79
53	7.0	2.96	1.41	-
68	7.0	2.31	1.57	9.47
83	7.3	2.51	1.53	7.34
98	7.5	4.00	1.78	9.89

Table 4. Field and Analytical Data from Core IV

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	67.2	1.5	2.4	.27	.23	1.18	.99	24.6
23	67.3	1.0	2.6	.29	.22	.97	.75	26.9
38	64.9	2.0	4.1	.21	.17	.91	.72	26.1
53	65.0	8.5	5.8	.25	.20	1.20	.96	25.8

Depth in Cm	PH	Phosphate Fractions in moles/gram		
		$Al\text{-}PO_4$	$Fe\text{-}PO_4$	$Ca\text{-}PO_4$
8	5.8	4.14	1.76	3.82
23	6.8	3.63	1.40	1.77
38	6.7	2.99	.97	5.61
53	6.7	3.62	2.83	4.57

Table 5. Field and Analytical Data from Core V

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	50.3	3.5	1.5	.21	.32	.44	.66	13.8
23	40.6	8.5	4.5	0	0	-	-	11.7
38	42.5	12.3	5.4	.12	.13	.48	.50	19.7
53	50.3	15.5	6.3	.18	.20	.53	.58	19.0
68	44.8	17.7	7.1	.20	.26	-	-	16.2
83	44.6	16.2	7.5	.16	.30	.42	.80	10.9
98	39.1	21.0	12.3	.11	.20	.99	.75	11.7
113	34.9	19.0	8.2	.14	.31	.22	.49	9.4

Depth in Cm	PH	Phosphate Fractions in moles/gram		
		$Al-PO_4$	$Fe-PO_4$	$Ca-PO_4$
8	7.2	2.00	0.93	12.15
23	7.3	2.63	0.73	21.05
38	7.3	3.04	0.86	12.90
53	7.3	2.54	0.96	11.54
68	7.3	2.27	0.84	13.07
83	7.4	1.57	1.15	20.84
98	7.5	3.05	1.38	13.76
113	7.5	1.89	0.73	20.32

Table 6. Field and Analytical Data from Core VI

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	51.8	25.8	1.2	.03	.06	.17	.34	10.5
23	-	8.2	3.1	-	-	-	-	-
38	26.0	8.5	4.1	.02	.06	.22	.69	6.6
53	28.4	8.2	3.5	.01	.05	.25	.18	4.4
68	-	6.7	2.0	-	-	-	-	-
83	33.3	7.5	4.5	.06	.05	.51	.51	28.8

Depth in Cm	PH	Salinity in 0/00	Phosphate Fractions in moles/gram		
			$Al\text{-}PO_4$	$Fe\text{-}PO_4$	$Ca\text{-}PO_4$
8	7.4	27.5	.75	1.18	11.87
23	7.7	28.5	-	-	-
38	7.6	33.5	1.35	.88	14.22
53	8.1	24.0	1.20	.31	12.47
68	7.5	26.0	-	-	-
83	7.8	33.5	1.65	.83	8.98

Table 7. Field and Analytical Data from Core VII

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	63.0	Trace	Trace	-	-	-	-	-
23	61.8	Trace	Trace	.09	.07	.64	.49	26.9
38	68.2	Trace	0.2	.13	.09	.68	.49	28.6
53	-	Trace	0.4	-	-	-	-	-
68	63.2	Trace	0.3	.10	.08	.66	.51	26.9
83	58.9	Trace	2.0	.13	.09	.88	.64	28.2
98	-	Trace	2.4	.15	.11	.76	.58	27.3

Depth in Cm	PH	Salinity in 0/00	Phosphate Fractions in moles/gram		
			$Al\text{-}PO_4$	$Fe\text{-}PO_4$	$Ca\text{-}PO_4$
8	6.3	9.9	-	-	-
23	6.4	10.8	4.10	.67	2.14
38	6.3	12.6	4.34	2.39	2.15
53	6.3	11.3	-	-	-
68	6.2	13.5	3.46	3.44	2.89
83	6.7	17.0	3.68	3.15	3.36
98	7.5	17.5	3.15	2.73	4.94

Table 8. Field and Analytical Data from Core VIII

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	50.1	Trace	.02	.09	.07	.78	.60	27.0
23	55.8	1.5	.03	-	-	-	-	-
38	50.6	4.7	.03	.10	.08	.82	.66	25.5
53	-	14.8	.01	-	-	-	-	-
68	51.9	11.2	.02	.20	.26	1.01	1.29	16.2
83	-	12.8	.01	.23	.23	1.06	1.07	20.5
98	51.1	16.8	.03	.26	.23	.98	.86	23.6

Depth in Cm	PH	Salinity in 0/00	Phosphate Fractions in moles/gram		
			$Al\text{-}PO_4$	$Fe\text{-}PO_4$	$Ca\text{-}PO_4$
8	6.8	9.0	4.46	8.25	3.31
23	6.8	8.6	-	-	-
38	6.9	8.1	3.28	6.25	5.01
53	6.9	8.1	-	-	-
68	7.0	8.6	2.61	7.87	3.17
83	7.1	8.6	2.31	7.15	3.15
98	7.4	7.9	2.84	6.94	3.26

Table 9. Field and Analytical Data from Core IX

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	53.2	Trace	Trace	.12	.12	.83	.86	20.0
23	-	Trace	0.03	-	-	-	-	-
38	52.6	Trace	0.03	.15	.13	.77	.65	24.7

Depth in Cm	PH	Phosphate Fractions in moles/gram		
		$Al\text{-}PO_4$	$Fe\text{-}PO_4$	$Ca\text{-}PO_4$
8	4.6	1.24	1.61	.66
23	5.7	-	-	-
38	5.6	1.77	1.45	1.18

Table 10. Field and Analytical Data from Core X

Depth in CM	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
3	53.0	2.0	0	.32	.20	.69	.42	33.7
2	61.0	2.0	0.2	.31	.20	.87	.55	32.8
1	62.8	2.0	4.2	.11	.08	.73	.53	28.6

Depth in Cm	PH	Salinity in 0/00	Phosphate Fractions in moles/gram		
			$Al-PO_4$	$Fe-PO_4$	$Ca-PO_4$
8	6.6	23.5	3.89	7.56	6.94
23	6.4	23.5	3.16	4.56	3.16
38	6.4	23.5	-	-	-

Table 11. Field and Analytical Data from Core XI

Depth in CM	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	60.2	2	0.5	-	-	-	-	-
23	61.6	3.5	4.8	-	-	-	-	23.3
38	61.0	2	6.1	.11	.12	.59	.62	19.6
53	62.2	2.5	6.4	.11	.11	.78	.77	20.9
68	61.8	4.5	8.6	.09	.10	.68	.74	19.0
83	61.3	7	6.2	.17	.17	.56	.55	20.9
98	61.1	8	9.4	.17	.13	.61	.47	26.8
113	65.1	10	9.4	.20	.16	.68	.53	26.4
128	64.8	16.5	8.4	.20	.15	.61	.46	27.1
143	63.0	14	11.6	.21	.17	.53	.44	25.2

Depth in Cm	PH	Salinity in 0/00	Phosphate Fractions in moles/gram		
			$Al\text{-}PO_4$	$Fe\text{-}PO_4$	$Ca\text{-}PO_4$
8	6.6	28.5	-	-	-
23	6.6	25.0	2.75	2.03	2.03
38	6.6	27.5	2.84	2.01	2.92
53	6.6	26.0	2.51	2.66	3.50
68	6.7	30.0	3.05	2.21	2.73
83	6.7	31.0	3.39	1.98	3.24
98	6.7	28.5	3.46	1.21	2.92
113	6.9	30.0	3.05	1.36	3.89
128	6.9	37.5	2.38	1.66	4.48
143	6.9	35.0	3.26	1.68	4.00

Table 12. Field and Analytical Data from Core XII

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	49.1	0	1.7	.11	.10	.56	.52	22.2
23	56.0	0	1.6	.09	.08	.47	.39	25.0
38	61.5	0	3.8	.07	.06	.45	.36	26.0
53	56.6	Trace	5.6	.07	.05	.52	.40	27.0
68	59.2	1.5	5.0	.06	.13	.43	.95	9.4

Depth in Cm	PH	Salinity in 0/00	Phosphate Fractions in moles/gram		
			$Al-PO_4$	$Fe-PO_4$	$Ca-PO_4$
8	-	-	2.77	2.03	1.72
23	6.5	16.5	2.00	1.01	7.82
38	6.7	22.5	1.68	0.34	7.05
53	6.6	25.0	2.42	0.34	6.63
68	6.5	27.5	1.40	0.93	11.79

Table 13. Field and Analytical Data from Core XIII

Depth in Cm	Per Cent Water	Composition of Interstitial Waters in PPM		Exchangeable NH_4 in meq/100 gm		Fixed NH_4 in meq/100 gm		Cation Exchange Capacity in meq/100 gm
		NH_4	PO_4	Bulk	Norm	Bulk	Norm	
8	53.2	0	4.5	.03	.02	.72	.59	25.3
23	54.8	-	-	.06	.06	.87	.83	21.8
38	45.1	1	6.9	.06	.05	1.00	.78	26.6
53	51.0	2	8.2	.03	.03	.57	.61	19.4
68	44.1	3	9.9	.05	.24	.43	2.03	4.4
83	43.3	4	13.8	.03	.05	.34	.54	13.1
98	46.7	5.5	15.5	.02	.04	.51	.95	11.1
113	52.1	6	16.5	.05	.05	.63	.62	21.2
128	60.8	7.5	15.5	.04	.03	.31	.22	29.2
143	66.5	7	13.8	.05	.05	.64	.60	22.1
158	64.0	9.5	16.5	.08	.07	.60	.53	23.2

Depth in Cm	PH	Salinity in 0/00	Phosphate Fractions in moles/gram		
			$Al-PO_4$	$Fe-PO_4$	$Ca-PO_4$
8	-	-	2.33	1.75	2.58
23	6.6	24.5	3.82	2.56	3.10
38	6.6	22.5	3.60	1.80	3.44
53	6.7	27.5	2.21	1.47	8.10
68	6.7	23.5	2.21	1.47	10.42
83	6.7	27.5	1.47	3.68	10.73
98	6.8	31.0	3.15	1.89	9.89
113	6.6	33.5	2.27	1.45	8.14
128	6.8	26.0	1.47	0.63	10.95
143	6.8	30.0	2.21	1.05	8.63
158	6.8	32.0	2.10	2.31	9.58

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